

1

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DYEABLE POLYPROPYLENE FIBERS CONTAINING POLYVINYL ACETAL RESINS

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This invention relates to polypropylene fibers. More particularly, this invention relates to substantially crystalline polypropylene fibers which exhibit excellent dye affinity, fastness properties and resistance to oxidation as well as good resistance to weathering. In a more specific aspect, this invention relates to polypropylene fibers which are modified with polyvinyl acetal resins.

It is well-known that polypropylene, particularly the polypropylene which is partially or completely crystalline, can be spun into synthetic fibers having unusual physical properties. This polymer is, however, subject to inherent disabilities which greatly restrict its utility in the fabrication of general purpose fibers. For example, a high-molecular-weight, fiber forming, crystalline polyolefin such as polypropylene, is a relatively insoluble, chemically inert, hydrophobic material. Since it is not readily permeable to water, it cannot be dyed satisfactorily by the ordinary dyeing procedures. Since it is relatively inert chemically, it cannot be permanently dyed even with hydrocarbon soluble dyestuffs. Furthermore, substantially crystalline polypropylene yarns and fibers cannot be dyed readily with a wide variety of dispersed and premetalized dyes nor can such yarns and fibers be dyed to deep shades having good light and gas fastness. Moreover, the susceptibility of polypropylene fibers to oxidative degradation, instability toward ultraviolet light and poor weathering characteristics have further limited their utility. Hence, it is most desirable to obtain fibers free from the above-mentioned disabilities in order to increase their value in the textile field.

The problem of obtaining polypropylene fibers having the high tenacity, low elongation and other excellent properties characteristic of such fibers without the accompanying undesirable limitations described above, has plagued prior art workers in this field for many years. However, with the development of the instant invention, we have been able to furnish such a polypropylene fiber.

Accordingly, it is an object of this invention to provide polypropylene fibers having improved dye affinity.

Another object of this invention is to provide polypropylene yarns and fibers with greatly improved dyeing characteristics so that they can be dyed readily with a wide variety of dispersed and premetalized dyes which normally will not dye unmodified polypropylene.

Another object is to provide partially or completely crystalline polypropylene yarn and fibers which can be dyed to deep shades with excellent light and gas fastness.

Still another object of this invention is to provide polypropylene yarns and fibers having improved resistance to oxidation and weathering in addition to excellent physical properties.

Further objects of the invention will become apparent throughout the following description.

In accordance with this invention it has been found that polymeric blends of polypropylene and an effective concentration of about 1 to about 25% and more preferably about 5 to about 15%, by weight, based on the blend, of one or more of the polyvinyl acetal resins as hereinafter described, can be spun into high strength fibers and yarns having the same percentage composition which exhibit excellent dye affinity for dispersed and premetal-

2

ized dyes. The dyed materials obtained thereby exhibit excellent light and gas fastness and unexpectedly good oxidative stability.

Although unmodified polypropylene shows virtually no affinity for dyestuffs, it can be dyed with some dyes to weak shades having, however, very poor fastness properties as mentioned hereinbefore. Surprisingly, it has been found that the shades produced by a given dye on the unmodified polypropylene yarn and on the modifiers themselves was quite different from the shades produced by the same dye on the modified polypropylene yarns of this invention. This unpredictable result indicates that the fibers spun from the polymeric blends described above possess characteristics which ordinarily would not have been expected in fibers spun from simple mixtures of polymeric materials. In this connection, it was also discovered that the modified polypropylene fibers described herein were more resistant to oxidative degradation than fibers obtained from unmodified polypropylene.

The modified polypropylene fibers of this invention are also more stable toward ultraviolet light and weathering conditions than unmodified polypropylene fibers. The reason for the increased stability of the modified polypropylene fibers toward oxidation, light and weathering is not completely understood. It is possible, however, that free radicals generated from the polymeric modifiers combine with free radicals produced from the polypropylene to prevent chain reactions which would otherwise result in rapid deterioration of the polyolefin. It is possible that the polymeric modifiers may also be effective in absorbing actinic radiant energy which otherwise could activate free-radical mechanism of decomposition in the polypropylene.

The modified polypropylene fibers and yarns may be further stabilized against thermal breakdown and weathering with any of the conventional stabilizers for polyolefins. It is usually convenient to add such stabilizers to the polymeric blends before spinning into fibers.

The modifiers polypropylene fibers and yarns of this invention may be drawn to give the same high tenacities, low elongations and other excellent properties found in unmodified polypropylene fibers and yarn. This is quite surprising, since the polyvinyl acetals are substantially noncrystalline when prepared by conventional methods and, as a result, give fibers which possess low tenacities, high shrinkage properties, and no commercial value. It would have been predicted, contrary to fact, that these materials, when used to modify polypropylene for fibers and yarn, would have deleteriously affected the properties of the yarn.

The polyvinyl acetal resins employed in this invention are well known materials, typically derived by conventional methods from polyvinyl acetates by hydrolysis of the latter material, followed by reaction with an aldehyde. As is explained by Schildknecht in "Vinyl and Related Polymers," published by John Wiley and Sons, Inc., New York, N.Y., in 1952, at page 358, high-polymer chemists use the term "polyvinyl acetal" to indicate polyvinyl alcohols which have had a major part of their hydroxyl groups condensed with aldehydes. One mole of the aldehyde condenses with two hydroxyls to yield the acetal. The remaining hydroxyl groups may be free or they may be acylated.

Any polyvinyl acetal resin can be used in the practice of our invention although it is desirable that the material be a polyvinyl acetal resin of an aldehyde of 1 to 18 carbon atoms. Also, it is preferred that the resin contain from about 50 to about 100 mole percent of vinyl acetal groups derived from the afore-mentioned aldehydes or mixtures thereof, the balance of the polyvinyl alcohol hydroxyls being free or acylated. The resins employed herein have molecular weights of at least 1,000 and in-

3

clude, for example; polyvinyl acetaldehyde acetal, polyvinyl n-valeraldehyde acetal, polyvinyl formaldehyde acetal, polyvinyl butyraldehyde acetal, polyvinyl heptaldehyde acetal and the like.

Various aldehydes can be employed in the formation of the polyvinyl acetal resins of this invention, as indicated above. Thus, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, hexaldehyde, benzaldehyde, crotonaldehyde, heptaldehyde, pelargonic aldehyde, dodecanaldehyde, margaric aldehyde, octadecanaldehyde and the like and mixtures thereof can be employed. In general, polyvinyl acetal resins made from saturated lower aliphatic aldehydes are preferred. In particular, polyvinyl acetal resins made with saturated aliphatic aldehydes containing 8 or less carbon atoms, and especially those made with formaldehyde, acetaldehyde and butyraldehyde and mixtures thereof are preferred.

It has been found that blends of crystalline polypropylene with the polymeric modifiers described can be melt spun into high strength yarns which can be dyed to deep, light and gas fast shades by means of dispersed and premetallized dyes. The dyeing process can be carried out using conventional procedures either with or without carriers. The polypropylene blends can contain from 1% or less to 25% or more, by weight of the polyvinyl acetal modifier, although the preferred concentration of modifier is from 5 to 15%. However, there are special situations which may warrant the use of 30 or perhaps even 40% by weight based on the blend, of certain of the modifiers disclosed. Furthermore, even though as little as 1% by weight based on the blend, of the specified polymeric modifiers will impart dye affinity to the fibers, it is preferred that amounts of at least 5% be employed, particularly where deep shades are desired. Polypropylene blends of this type can be melt spun at temperatures ranging from 25 to 65° C. lower than are necessary to melt spin pure polypropylene.

Blends of crystalline polypropylene with one or more of the polymeric modifiers may be prepared in any desired manner, whether it be mechanical mixing, coprecipitation or other blending method, e.g., they can be prepared at elevated temperatures on rolls, in a Banbury mixer or any other suitable type of processing equipment or they can be prepared by multiple extrusion techniques. The polymeric modifiers can have a molecular weight of 1000 and higher depending on the particular blend properties desired and the blending method employed. It is to be understood, of course, that any polymeric modifier having a molecular weight in excess of 1000 which is capable of imparting the desired characteristics, as set forth herein, to polypropylene is within the scope of our invention.

Usually, it is preferable to prepare the modified polypropylene compositions from polypropylene having a conditioned density above 0.90 and an inherent viscosity in tetralin at 145° C. of from 0.9 to 1.2. Conditioned density, as used herein, refers to the density determined on a sample which has been annealed in an attempt to obtain maximum crystallinity. A conventional annealing procedure involves placing the sample in a tube, heating under high vacuum or in a nitrogen atmosphere to just below the softening point, and allowing the sample to cool slowly. Polypropylene having inherent viscosities above 1.2 can be used in preparing the modified compositions, but then it is usually necessary to degrade these compositions thermally to a lower viscosity in order to realize optimum melt spinning characteristics and fiber properties. The temperatures required for this degradation are usually above 300° C. and often result in an appreciable loss of modifier through depolymerization. Polypropylene of inherent viscosity less than 0.9 can be used in preparing modified compositions for melt spinning, but it does not afford fibers having optimum physical properties.

The modified polypropylene compositions described herein may be spun into fibers having the desired characteristics by the conventional spinning procedures, e.g.,

4

melt spinning, dry spinning, wet spinning or extrusion through a suitable die. Furthermore, these modified polypropylene compositions can be formed into the various cross-sections, e.g., cloverleaf, Y-section etc., by employing spinnerettes or dies having appropriately shaped orifices.

The preparation of typical polypropylene blends and fibers embodying this invention is illustrated in the following examples, but it will be understood that the examples are merely illustrative and not intended to limit the scope of the invention unless otherwise indicated.

Example 1

Several compositions comprising crystalline polypropylene (inherent viscosity=1.0 and density=0.912) and polyvinyl acetaldehyde acetal were prepared by mechanically blending pellets of the two polymeric materials followed by melt extrusion and repelleting of the resulting compositions. The polyvinyl acetaldehyde acetal was prepared by replacement of 70% of the acetyl groups in poly(vinyl acetate) by acetaldehyde. The modified polypropylene compositions were melt spun into 34-filament yarns having the properties shown below. Knit tubes prepared from these yarns all dyed to deep shades with dispersed dyes such as 4-(4'- β -hydroxy-ethyl-anilino)-5-nitro-1,8-dihydroxy-anthraquinone, 2-nitro-4-sulfonamido-4'-ethoxydiphenylamine and amyl-4-(1'-amino-2'-methoxy-anthraquinonyl) carbamate in the aqueous dye baths at boil for one hour. Even deeper shades were obtained by using carriers such as benzyl n-butyrate. All samples showed excellent fastness to ultraviolet light in a fadeometer for 20 hours.

	I	II	III	IV	V
Polypropylene, percent.....	100	95	90	85	80
Poly(vinyl acetal), percent.....	0	5	10	15	20
Yarn Viscosity.....	0.93	1.00	0.90	1.06	0.82
Total Denier.....	223	150	184	223	216
Tenacity, g./den.....	7.33	7.42	6.86	6.60	5.07
Elongation, percent.....	18	13	13	23	15
Elastic Modulus, g./den.....	63	97	87	56	76

Similar results were obtained from a polyvinyl acetal containing 50% vinyl acetal groups derived from n-valeraldehyde, 35% vinyl acetate groups and 15% vinyl alcohol groups.

Example 2

A mixture of 9 parts of crystalline polypropylene (inherent viscosity=1.05 and density=0.914) and 1 part of poly(vinyl formal) containing 79 mole percent of vinyl formal groups and 21 mole percent of vinyl alcohol groups was prepared by blending granules of the two resins. This mixture was then melt extruded into 1/8-in. rod and then was chopped into pellets having a length of about 1/8-in. The resulting composition was readily melt spun into 34-filament yarn at a spinning temperature of 260° C. The unmodified polypropylene required a melt spinning temperature of 280° C. for optimum spinning characteristics. The modified polypropylene yarn obtained above was knitted into a "sock" or tube which was used in dyeing tests. Excellent dye affinity for dispersed dyes was demonstrated by the deep shades obtained with 4-(4'- β -hydroxyethyl-anilino)-5-nitro-1,8-dihydroxy-anthraquinone and amyl-4-(1'-amino-2'-methoxy-anthraquinonyl) carbamate.

Other poly(vinyl formal) resins which would be used with equally good results were those containing from 5 to 20% of vinyl alcohol groups or vinyl acetate groups or a combination of these groups.

Example 3

Blends of crystalline polypropylene with poly(vinyl butyral) were prepared by melt extrusion of the mechanical mixtures of the two resins. The poly(vinyl butyral) contained 80% vinyl butyral groups, 19% vinyl alcohol groups and 1% vinyl acetate groups. The above blends

5

were melt spun into 34-filament yarns having the properties shown below:

	I	II	III
Polypropylene, percent.....	96.5	88	75
Poly(vinyl butyral), percent.....	3.5	12	25
Yarn Viscosity.....	1.07	0.92	0.88
Total Denier.....	154	160	199
Tenacity, g./den.....	8.22	7.08	5.71
Elongation, percent.....	17	20	19
Elastic Modulus, g./den.....	89	81	58

Knit tubes made from these yarns were readily dyed with 4-(4'- β -hydroxyethylanylino)-5-nitro-1,8-dihydroxy-anthraquinone, amyl-4-(1'-amino-2'-methoxy-anthraquinonyl) carbamate and 2-nitro-4-sulfonamido-4'-ethoxydiphenylamine. Deep shades which were both light- and gas-fast were easily obtained.

Polyvinyl isobutyraldehyde acetal could be used in place of the poly(vinyl butyral) above with comparable results.

Example 4

The procedure of Example 2 was followed using a polyvinyl heptaldehyde acetal (containing about 35% vinyl alcohol groups and about 5% vinyl acetate groups) in place of the poly(vinyl formal). The yarn obtained showed a maximum tenacity of 6.8 g./den. and could be dyed readily with dispersed dyes to deep shades with good light fastness.

Polyvinyl acetals from pelargonic aldehyde, margaric aldehyde and oleic aldehyde gave similar results when used in place of the polyvinyl heptaldehyde acetal above.

Example 5

The procedure of Example 3 was followed using polyvinyl propionaldehyde acetal in place of the poly(vinyl butyral). The polyvinyl propionaldehyde acetal contained 90% vinyl propional groups and about 10% vinyl alcohol groups. Strong yarns having tenacities of 4.9 to 7.5 g./den. were obtained. All of these yarns dyed to deep shades with dispersed dyes.

Example 6

A mixed polyvinyl acetal derived from polyvinyl alcohol and containing both vinyl acetaldehyde acetal groups (66%) and vinyl butyral groups (15%) was used in place of the poly(vinyl formal) in the procedure of Example 2. The modified polypropylene yarn obtained showed excellent affinity for dispersed dyes.

Thus, by means of this invention, substantially crystalline polypropylene yarns and fibers having improved dye affinity, excellent light and gas fastness and increased stability may be obtained. The improved polypropylene fibers of this invention may be used in the same manner as conventional polypropylene fibers; for example, they can be woven into wool-like blankets or used in the production of automobile seat covers and marine hawsers.

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. Polypropylene fiber exhibiting excellent dye affinity,

6

light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl acetal resin.

2. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 5 to about 15% by weight, based on the fiber, of a polyvinyl acetal resin.

3. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl acetal resin containing at least 50 mole percent acetal.

4. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl acetal resin containing at least 70 mole percent acetal.

5. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl acetal resin of an aldehyde containing 1 to 18 carbon atoms.

6. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl acetal resin of an aldehyde containing 1 to 8 carbon atoms.

7. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl formaldehyde acetal resin.

8. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl acetaldehyde acetal resin.

9. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl propionaldehyde acetal resin.

10. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl butyraldehyde acetal resin.

11. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of a polyvinyl valeraldehyde acetal resin.

12. As a composition of matter, a blend comprising solid polypropylene containing about 1 to about 25% by weight, based on the blend, of a polyvinyl acetal resin.

13. As a composition of matter, a blend comprising solid polypropylene containing about 1 to about 25% by weight, based on the blend, of a polyvinyl acetal resin containing at least 50 mole percent acetal.

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